

Durability Studies: Gasoline / Reformate Durability

2002 National Laboratory R&D Meeting DOE Fuel Cells for Transportation Program

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Technical Objectives:

Examine Fuel Effects on FP/Stack Durability

**(Durability, Cold Startup,
Transients, Catalyst loading, NH₃)**

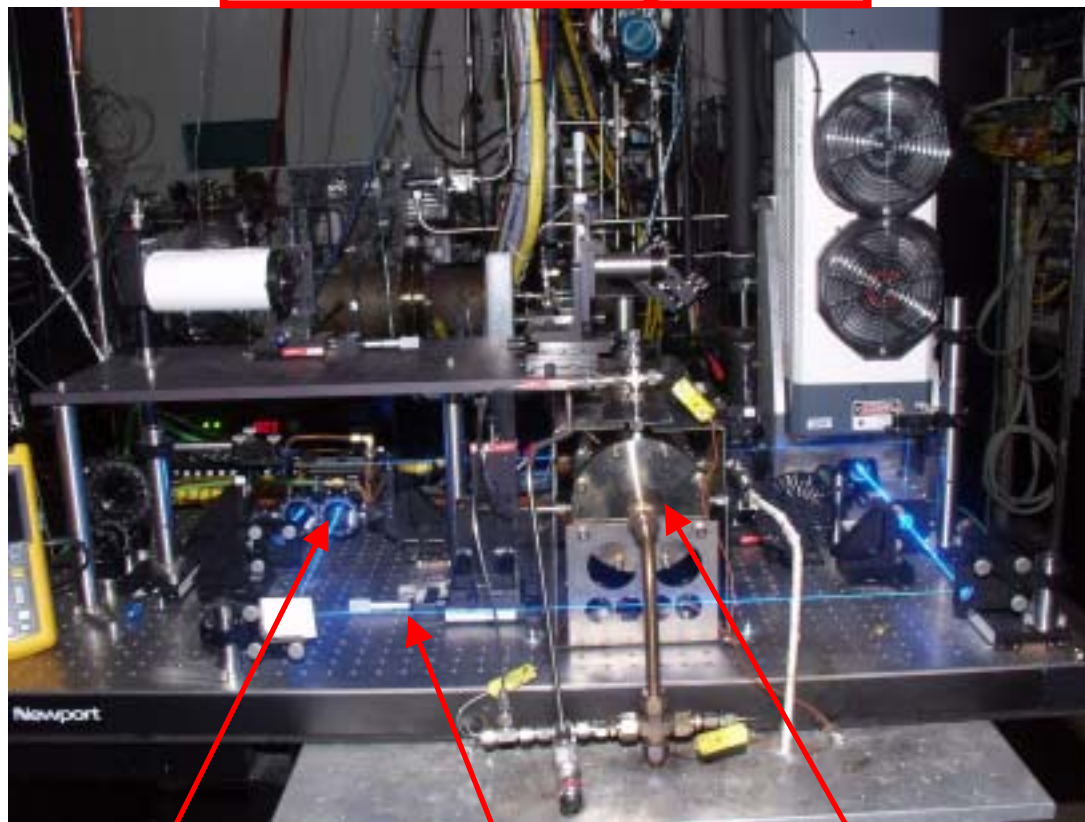
- Quantify fuel effects on durability (and performance).
 - Fuel composition effects
 - Fuel additive effects
 - Fuel impurity effects
- Identify chemical species limiting durability either in fuel processor or fuel cell stack.
- Understand the parameters that affect fuel processor and stack lifetime and durability.
 - Fuel processor catalyst durability
 - Fuel cell stack durability

Approach to Durability Studies

- Stack (single cell) Durability with Reformate
- Measure and identify chemical species ('known' poisons)
 - Carbon
 - Ammonia
 - Hydrocarbons
- Compare fuels and reactor conditions on performance (durability):
 - fuel components
 - fuel impurities
 - fuel additives (anti-oxidants, detergents) - N,N' – di-sec-butyl-p-phenylene diamine
- Monitor performance of Fuel Processor & single cell fuel cell
 - Catalyst degradation
 - MEA degradation
 - Carbon formation modeling
 - Equilibrium modeling / Thermodynamic property modeling
 - Modeling of energy required for start-up for various fuels

in situ Carbon Formation Laser Optics

MDL ~ 0.6 mg/min.

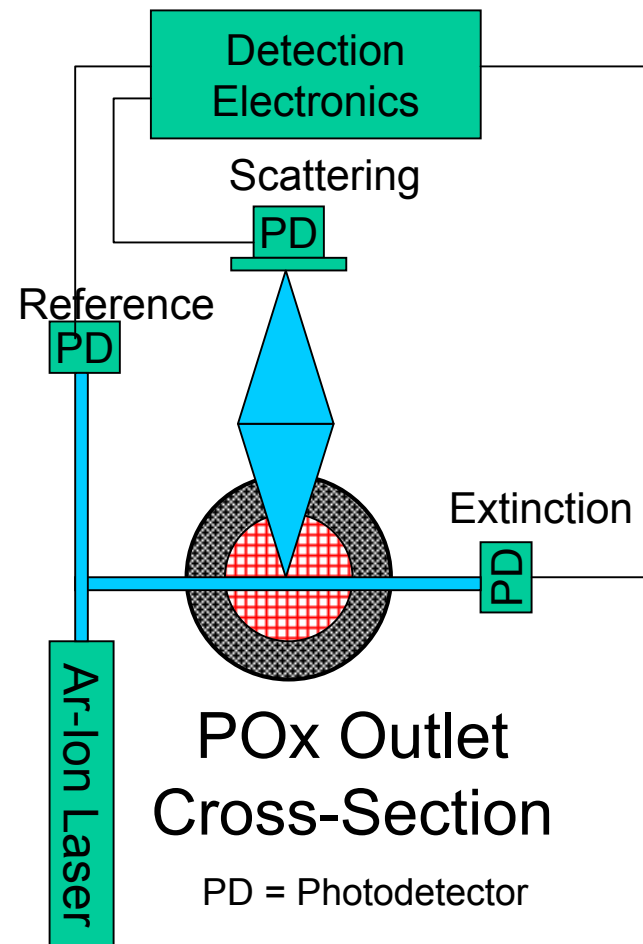


Signal
Detector

Reference Beam

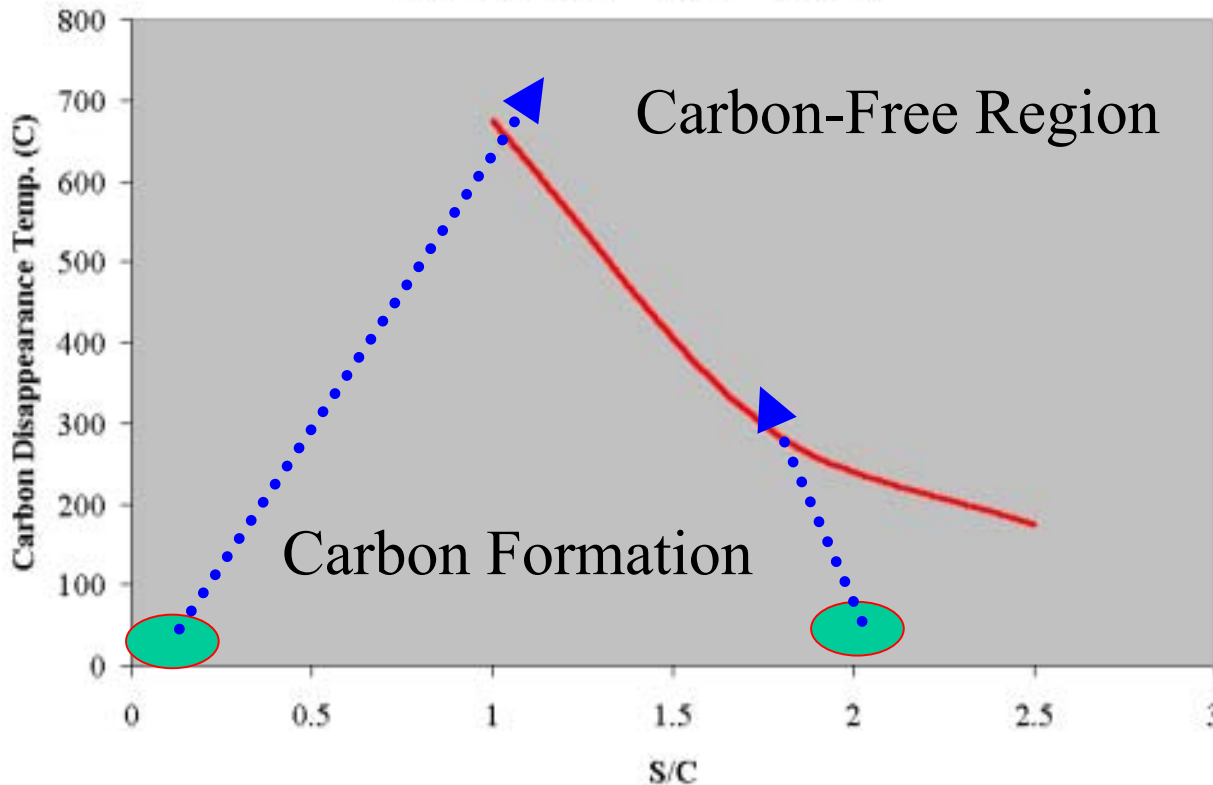
Reactor

Fuel Cell Program



Equilibrium Modeling

Gasoline: O/C = 0.6, P = 15 psig



Equilibrium defines fuel processor operating conditions

At start-up of fuel processor, water availability is questionable (freezing conditions)

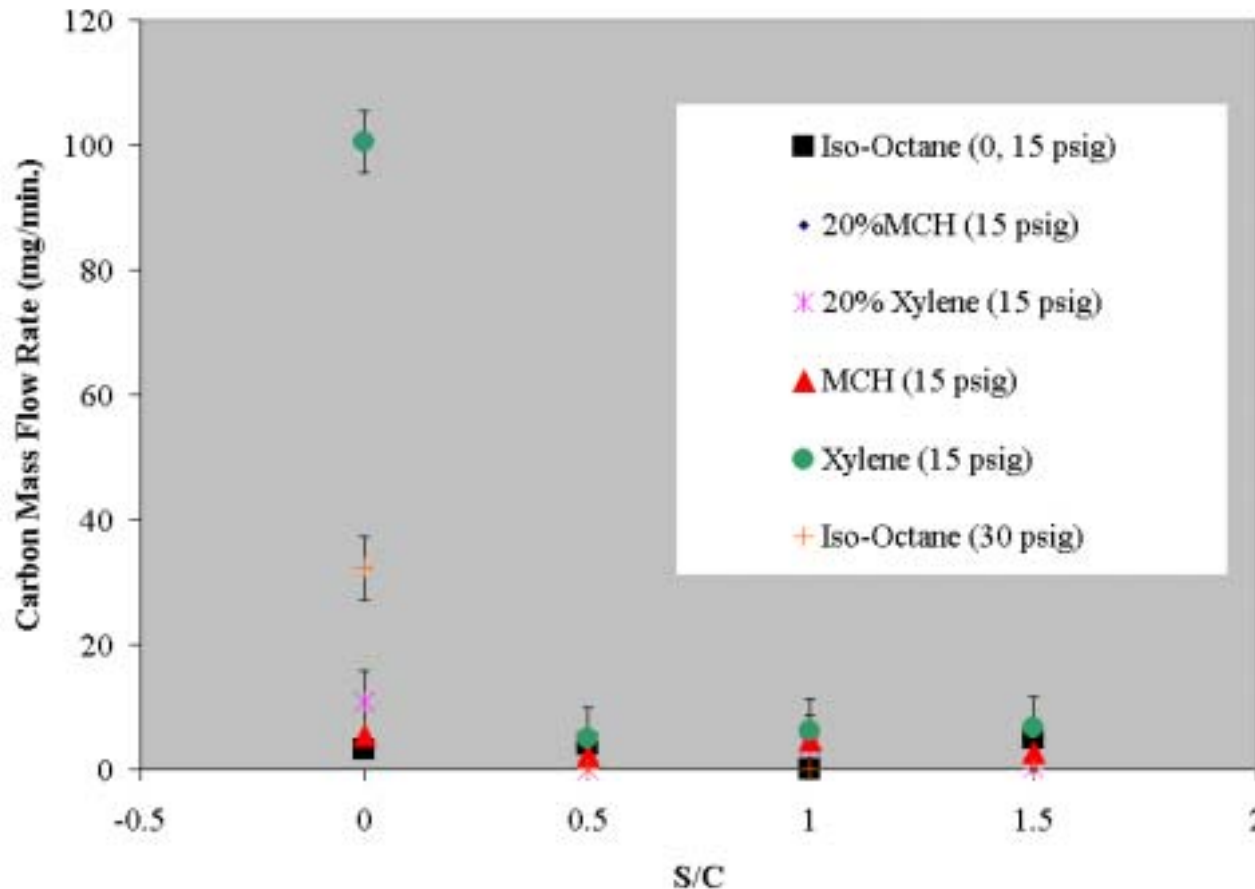
Avoiding zero equilibrium carbon will be difficult whether water is available or not.

At high S/C during start-up, during transition to carbon-free region - carbon formation kinetics appear low

Carbon Mass Flow Rate

$O/C = 0.65$

30 kW, 15 psig

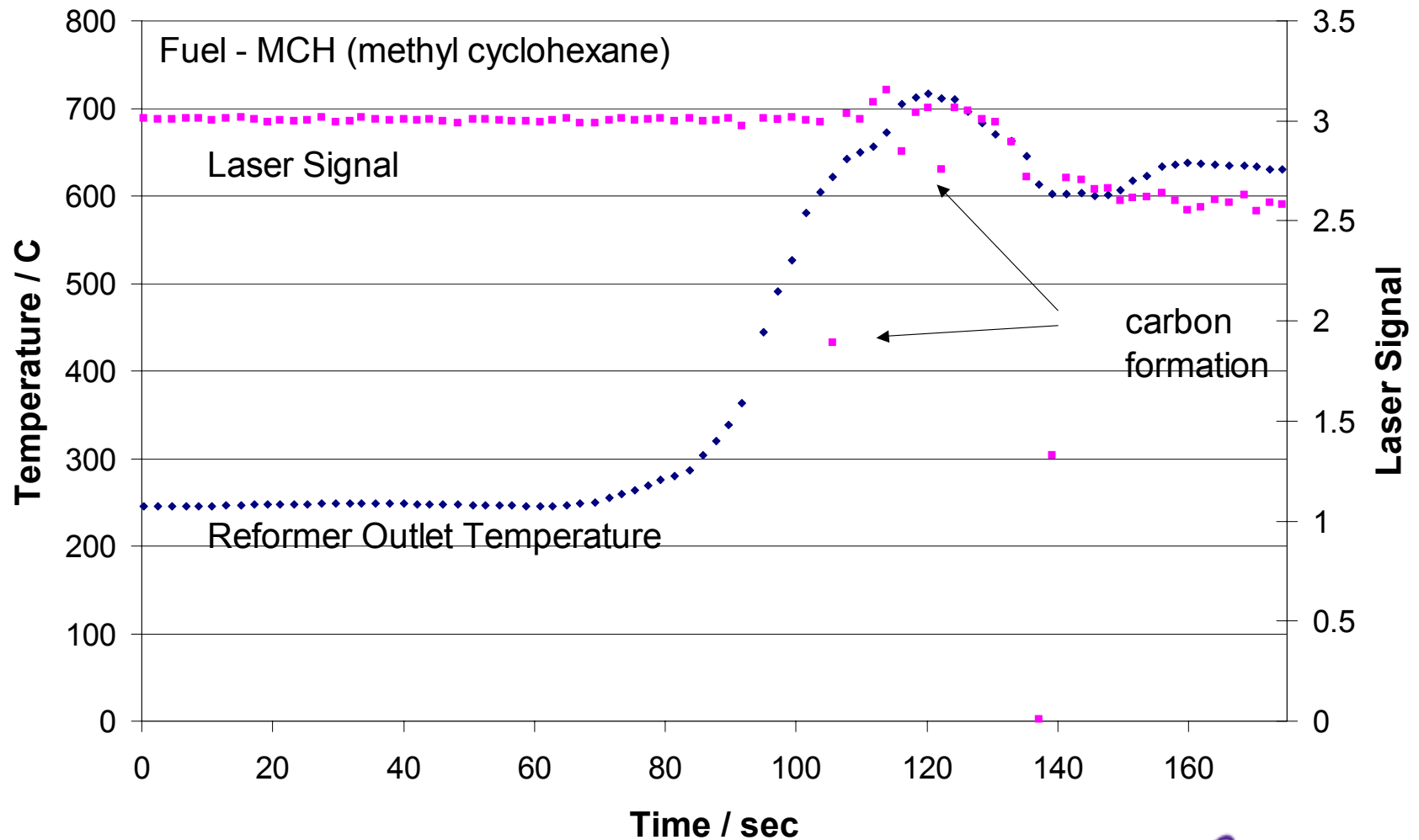


Saturated hydrocarbons with noble metal catalysts, and short residence times show little (no) carbon formation, even when carbon formation is predicted.

Fuel, catalyst and residence time have all been noted to have effects on carbon formation.

No change detected with 50 ppm N,N' – di-sec-butyl-p-phenylene diamine

Carbon Formation During Start-up

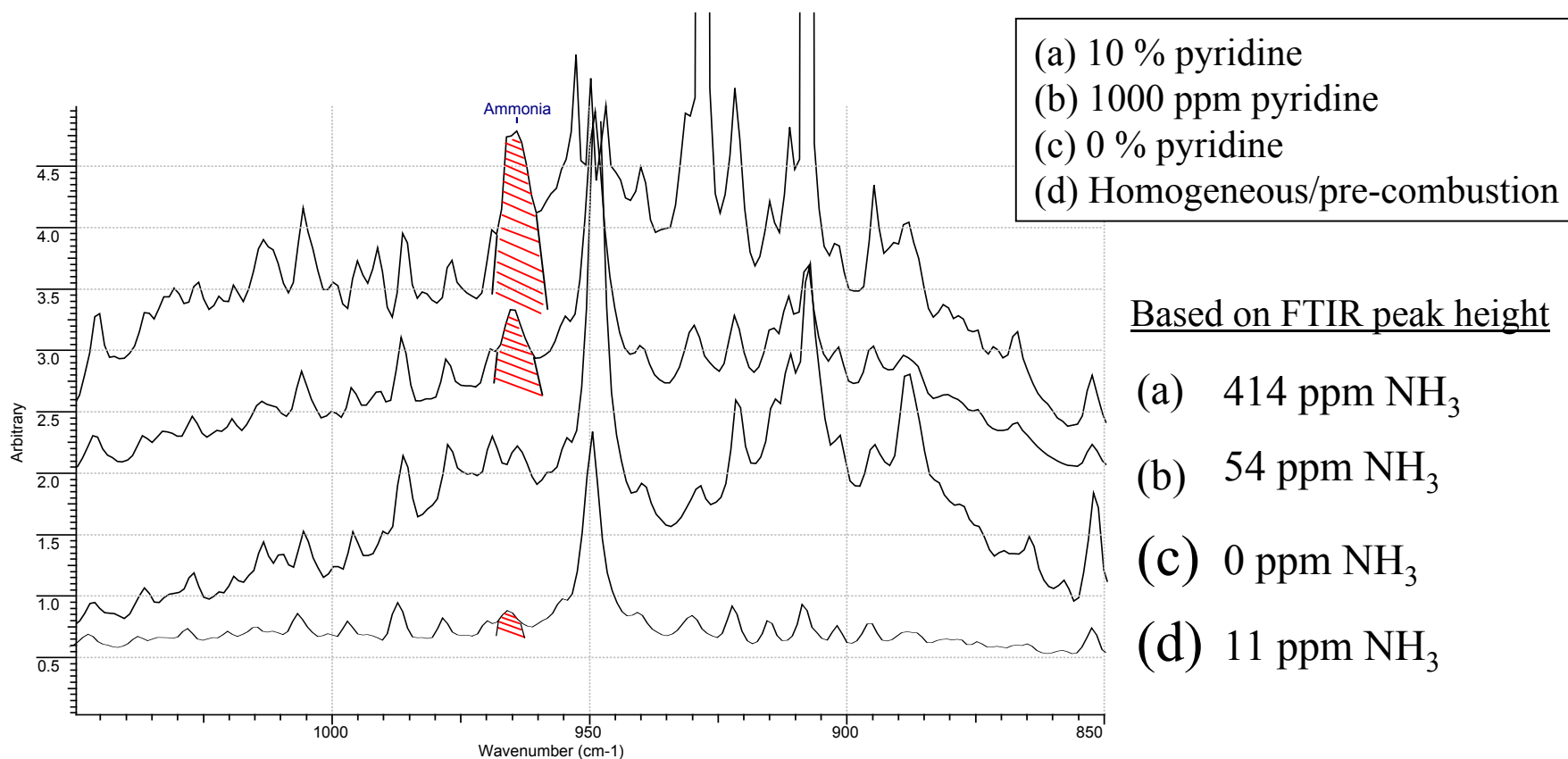


Ammonia formation from N-containing hydrocarbons

FTIR Spectra

Fuel: Methyl-cyclohexane

Catalytic partial oxidation with pure fuel components shows no NH_3 formation



- No NH_3 detected with 50 ppm $\text{N,N}'$ – di-sec-butyl-p-phenylene diamine

Gasoline Fuel Processor / Stack Durability Test Fixture



Fuel processor and fuel processor catalyst durability

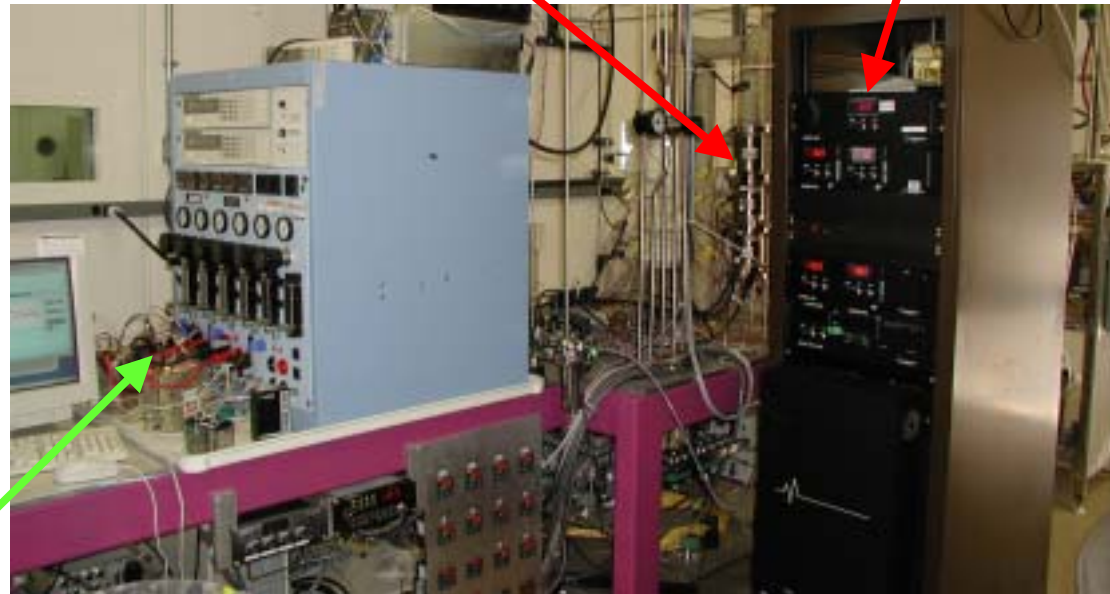
Side-by-side comparison of reformate and hydrogen durability

Single cell fuel cells operating from:

- reformate
- hydrogen

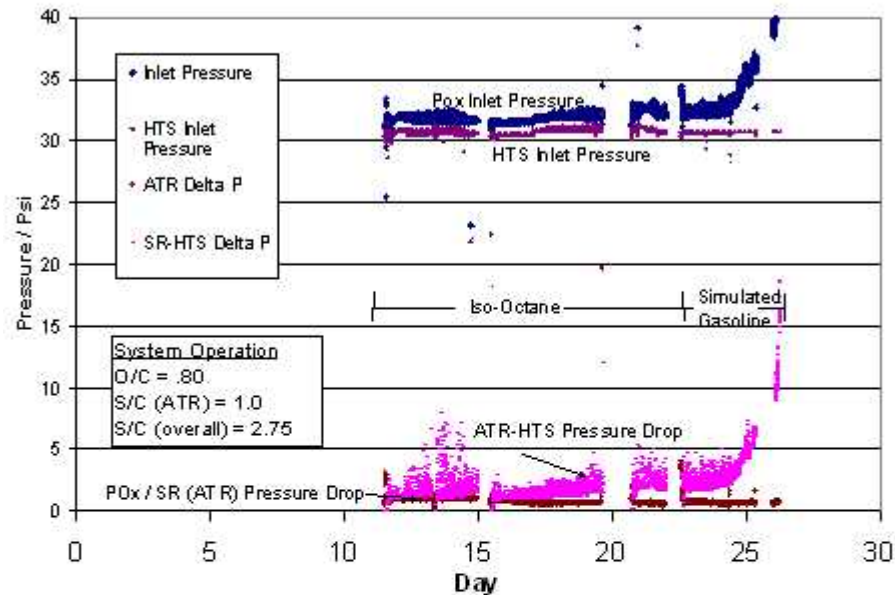
Gasoline Fuel Processor

Gas Analysis



Single Cells

Fuel Processor Train Durability



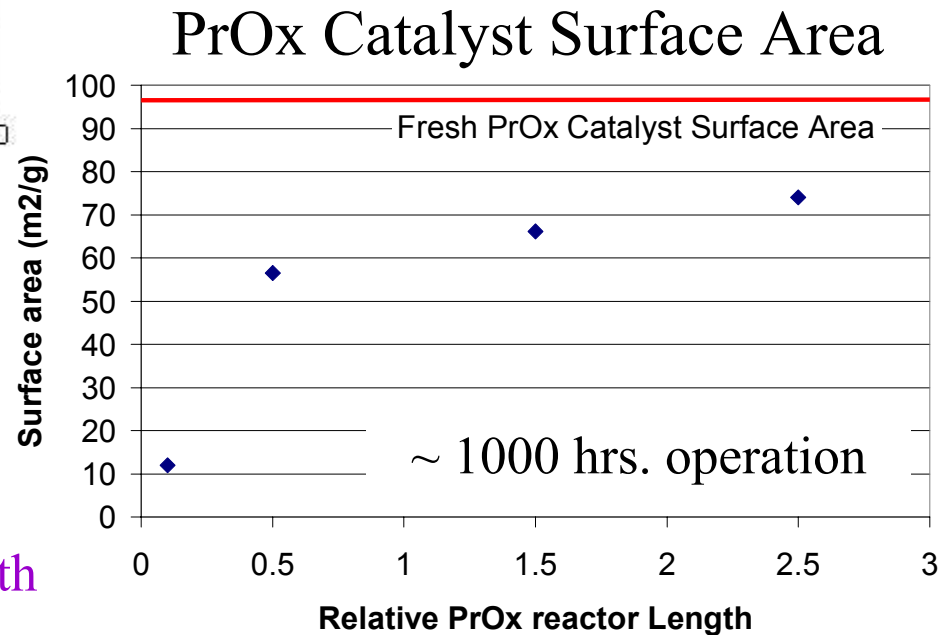
Carbon build up observed in between ATR and HTS when fuel was switched to 20 % aromatic fuel

- modified system to prevent carbon formation

Total hours on fuel processor system
~ 1000 hrs.

Initial testing on simulated fuels
due to fuel availability

See rapid degradation of single cell with
reformate (due to HC's?).



2001 Fuel Cell Review Comments

- Comments

- Make duration testing focal point of the program
- Series of comments about studying ATR's with incomplete oxygen conversion, and project is just iterative reactor design
 - we are not studying ATR's – we are studying fuels effects
 - purpose of study is to increase knowledge base on fuel effects, not to design reactors
 - differential reactors are normally used to determine kinetics
 - reactor normally has complete oxygen conversion, to achieve FY2001 results, ran at higher than normal space velocities to produce the results, so that the fuel component effect could easily be observed

Interactions/Collaborations

- National Technical Presentations
 - AIChE, ACS, ...
- Phillips Petroleum
 - providing fuel for testing
 - fuel formulations
- Delphi Automotive
 - discussions (~ reactor design, testing, diesel)
- CRADA Interactions
 - H₂ fuel
 - Motorola

Technical Progress Summary/Findings

- Carbon Formation

- Aromatics show high tendency for carbon formation
- Small amounts of carbon observed with non-aromatic compounds
 - little observed in areas even where equilibrium is favored
 - → residence time effect
- Carbon formation observed during start-up & during shut-down
- No observed effect by fuel detergent from initial investigation

- Ammonia formation

- Nitrogen from nitrogen-bound hydrocarbons form NH_3
- Little (no) NH_3 formation with catalytic processes
- Homogeneous/precombustion oxidation forms NH_3

- Fuel Processor / stack durability

- over 1000 hours operation on fuel processor
 - on-going characterization of catalyst / reformat
 - currently limited fuel cell operation with reformat

Future Plans

- Remainder of FY2002:
 - Hydrogen / gasoline reformat durability comparison
 - Carbon formation mapping
 - gasoline blends from Phillips
 - influence of additives and impurities including oxygenates
- FY > 2003:
 - Hydrogen / gasoline reformat durability comparison
 - Durability testing of fuel processing components
 - Fuel effect of reformat on fuel cell stack
 - Carbon formation during start-up and reactor transients
 - Carbon formation fundamentals:
 - Sulfur effect on carbon formation
 - delineate carbon formation mechanisms
 - kinetic expressions for carbon formation